PATENT SPECIFICATION (11) 1 514 651

1 514 651

(21) Application No. 20674/76 (22) Filed 19 May 1976
(23) Complete Specification filed 21 April 1977
(44) Complete Specification published 21 June 1978
(51) INT CL² C07D 401/12//C08K 5/34 (C07D 401/12, 213/72)
(52) Index at acceptance
C2C 1530 215 247 250 251 25Y 28X 311 313 31Y 322 32Y 332 337 456 45Y 470 611 620 631 670 671 680 698 775 776 793 797 79Y LP NG
C3K 210 220 221 271 274 283 PA

(72) Inventors ALAN FRANCIS HAWKINS, ROY DENNY BOWDEN and MICHAEL JOSEPH BROWN

(54) A 4,2'-BISPYRIDYLAMINE DERIVATIVE AND ITS USE IN MARINE COATING COMPOSITIONS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a new bispyridylamine derivative and its use in marine coating composition (or paints) suitable for application to surfaces to inhibit growth of marine or fresh water organisms thereon.

The formation of marine flora and fauna (e.g. alkae and barnacles) on the hull of a vessel increases the frictional drag between the hull and the water causing a fall in speed and an increase in fuel consumption. It is therefore common practice to apply "anti-fouling" paints to prevent the formation of the above organisms. The compositions of the present invention are especially applicable as marine anti-fouling compositions.

According to the present invention there is provided a new algicidal bipyridylamine derivative, namely 2,6 - difluoro - 3,5 - dichloro - 3',5' - dinitro - 6' - methyl - 4,2' - bispyridylamine.

This compound may conveniently be prepared by the treatment of 6 - amino - 2 - methyl - 3,5 - dinitropyridine with a base and reaction of the product with 2,4,6 - trifluoro - 3,5 - dichloropyridine.

A suitable base for use in the above reaction is sodium hydride, and the process may be carried out in a diluent or solvent, for example dimethylformamide.

The compound of the invention may also conveniently be prepared by the treatment of 2 - amino - 6 - methylpyridine with 2,4,6 - trifluoro - 3,5 - dichloropyridine in a suitable solvent, for example dimethylformamide, and then subjecting the intermediate product thus obtained to a nitration procedure, for example with a sulphuric acid/nitric acid mixture.

According to a further aspect of the present invention there is provided an anti-fouling coating composition comprising, as an active constituent, 2,6- difluoro - 3,5 - dichloro - 3',5' - dinitro - 6' - methyl - 4,2' - bispyridylamine.

2,6 - difluoro - 3,5 - dichloro - 3',5' - dinitro - 6' - methyl - 4,2' - bispyridylamine has a low solubility in water and a relatively high melting point, a high melting point being indicative of a reduced tendency to migrate towards the surface of the coating.

In order to improve the protection of the substrate against corrosion, the coating composition should preferably comprise a continuous layer of film-forming material; accordingly the coating composition preferably contains a film-forming material. The film-forming material may be a synthetic or a natural material or a mixture of such materials. Suitable synthetic materials include vinyl copolymers such as vinyl chloride/vinyl acetate/vinyl alcohol copolymers, phenolic resins, epoxy resins, polyurethanes and chlorinated synthetic rubber (for example 'Alloprene' R10). 'Alloprene' is a trade mark. Suitable natural materials include rosin and bituminous materials such as coal tar pitch. Preferably the coating composition after application and drying contains at least 10% by weight of film-forming material based on the total solids content of the composition.

The coating composition may also contain extenders and/or pigments, for example iron oxide, titanium dioxide, silica, and carbon black, and plasticisers, for example tricresyl phosphate or a chlorinated paraffin wax (for example 'Cereclor' 42). 'Cereclor' is a trade mark.

In addition to the above bispyridylamine

derivative, the composition may also contain other toxins known in the art; examples of such other toxins are cuprous oxide, zinc oxide, mercuric oxide, and trialkyl tin derivatives. A particularly suitable co-toxin is cuprous oxide.

Suitably the composition contains 5—70%, preferably 5—50%, for example 5—25%, by weight of the above bispyridylamine derivative based on the combined weight of the bispyridylamine derivative and the film-forming material.

The composition preferably contains a solvent for at least a part of the film-forming material, the solvent(s) evaporating once the composition has been applied to the surface. Suitable solvents include the aromatic hydrocarbons, ketones and esters.

The thickness of the film will depend on such factors as the nature of the ingredients and the duration of protection required, but thicknesses of 50 to 200 microns are generally suitable.

The composition can be applied to the surface by methods known in the art.

The invention is illustrated by the following Examples in which parts and percentages are by weight unless otherwise stated.

Example 1.

This Example illustrates the preparation of 2,6 - difluoro - 3,5 - dichloro - 3',5' - dinitro - 6' - methyl - 4,2' - bispyridylamine (I).

STAGE I

A solution of 2,4,6 - trifluoro - 3,5 - dichloropyridine (1.414 kg) in dry dimethylformamide (2.8 l) was added to a solution of 2 - amino - 6 - methylpyridine (756 g) in dry dimethylformamide (2.8 l) and the pale yellow solution was heated on a steam bath for 18 hours. After cooling to room temperature the solution was poured into *ca.* 20 l water when a white precipitate was formed, this was filtered off, washed with water and air-dried.

The crude material was recrystallised from industrial methylated spirit (12 ml/g) to yield 2,6 - difluoro - 3,5 - dichloro - 6' - methyl - 4,2' - bispyridylamine, m.p. 187—188°C (lit. 187—188°C).

STAGE II

2,6 - difluoro - 3,5 - dichloro - 6' - methyl - 4,2' - dispyridylamine (670 g) as prepared hereinabove was dissolved in concentrated sulphuric acid (3 l) and the solution cooled to 0°C. A nitrating mixture comprising concentrated nitric acid (185 ml) and concentrated sulphuric acid (185 ml) was added whilst keeping the temperature below 5°C. The solution was allowed to warm at room temperature over 1 hour and then was heated for 6 hours on a steam bath. The solution was cooled to room temperature and poured onto ice/water (*ca.* 30 l). A yellow solid precipitated, which was filtered off, washed with water and air-dried. This solid was dissolved in concentrated sulphuric acid (3 l) below 20°C and the solution cooled to 0°C. Concentrated nitric acid was added carefully and the temperature of the solution maintained at 5°C. After the addition the orange solution was allowed to stand for 16 hours at 20°C, and then poured into ice/water (30 l). A pale yellow solid was filtered off, washed with water and recrystallised from industrial methylated spirit to yield 2,6 - difluoro - 3,5 - dichloro - 3',5' - dinitro - 6' - methyl - 4,2' - bispyridylamine m.p. 117—119°C.

Analysis:

	C%	H%	N%
Required	34.8	1.32	18.4
Found	34.8	1.40	18.2

Example 2.

2,6 - difluoro - 3,5 - dichloro - 3',5' - dinitro - 6' - methyl - 4,2' - bispyridylamine incorporated in a paint composition, was tested as an anti-fouling agent. Polyvinyl chloride sheets were coated with paint compositions described below (Table 1) dispersed in 1:1 xylene : 'Aromasol' H as solvent ('Aromasol' is a trade mark). The paint thickness was 100 microns. The sheets were then exposed for 4 months to the sea on a raft. The sheets were arranged so that part of each sheet was above the water-line. Untreated sheets were similarly mounted and acted as control. The degree of fouling was estimated, using a scale of 0 to 10 where a score of 0 indicates that the sheet was fouled to the same extent as the control and a score of 10 indicates that no fouling occurred. Results are given in Table 2 for duplicate tests.

TABLE 1

Paint No.	Paint Composition (Parts by Volume)				
	Titanium Dioxide %	'Alloprene' R10 %	'Cereclor' 42 %	Rosin %	2,6-Difluoro-3,5-Dichloro-3',5'-Dinitro-6'-Methyl-4,2'-Bispyridylamine
1	45	16	4	10	25
2	20	40	10	25	5
3	35	16	4	40	5
4	30	26	6	22	16

TABLE 2

Paint No. (Table 1)	Time (Months)			
	1	2	3	4
1	8,8	9,9	8,7	9,9
2	1,1	0,0	0,0	0,1
3	3,1	1,1	0,0	0,-
4	7,7	7,7	7,3	8,9

Example 3.

The procedure of Example 2 was repeated using the paint compositions described in Table 3 in 1:1 xylene : 'Aromasol' H as solvent. All the test samples using the paint compositions shown in Table 3 were found to be completely free of any fouling (weed or animal) after immersion in the sea for 12 months.

TABLE 3

	PAINT COMPOSITION (Parts by Volume)					
Paint No.	Film-Forming Material	Pitch	Cuprous Oxide	Zinc Oxide	Tricresyl Phosphate	2,6-difluoro-3,5-dichloro-3',5'-dinitro-6-methyl-4,2'-dipyridylamine
5	('Alloprene' R10) 10	10	42.5	7.5	10	20
6	('Alloprene' R10) 11	11	46	8.0	4	20
7	(CPB) 14.5	3.5	47.6	8.4	6	20
8	(CPB) 22.5	3.5	55	0	12	5
9	(CPB) 18.5	4.5	38.25	6.75	20	12
10	(CPP) 20	5	41.65	7.35	6	20
11	(CPP) 14.5	3.5	47.6	8.4	6	20

CPB = Chlorinated polybutadiene

CPP = Chlorinated polypropylene

WHAT WE CLAIM IS:—

1. 2,6 - difluoro - 3,5 - dichloro - 3',5' - dinitro - 6' - methyl - 4,2' - bispyridylamine.

2. A method of preparation of 2,6 - difluoro - 3,5 - dichloro - 3',5' - dinitro - 6' - methyl - 4,2' - bispyridylamine which comprises treating 2 - amino - 6 - methylpyridine with 2,4,6 - trifluoro - 3,5 - dichloropyridine in a solvent medium, and subjecting the intermediate product thus obtained to a nitration procedure.

3. A method according to Claim 2 wherein the solvent is dimethylformamide.

4. A method according to Claim 2 or 3 wherein the nitration procedure comprises treatment with a sulphuric acid/nitric acid mixture.

5. A method of preparation of 2,6 - difluoro - 3,5 - dichloro - 3',5' - dinitro - 6' - methyl - 4,2' - bispyridylamine substantially as described with reference to Example 1.

6. An anti-fouling coating composition comprising, as an active constituent, 2,6 - difluoro - 3,5 - dichloro - 3',5' - dinitro - 6' - methyl - 4,2' - bispyridylamine.

7. A coating composition according to Claim 6 which contains a film-forming material.

8. A coating composition according to Claim 7 wherein the coating composition, after application and drying contains at least 10% by weight of film-forming material based on the total solids content of the composition.

9. A coating composition according to any of Claims 6 to 8 which contains a material acting as an extender and/or a pigment.

10. A coating composition according to any of Claims 6 to 9 which contains a plasticiser.

11. A coating composition according to any of Claims 7 to 10 wherein the composition contains from 5% to 70% by weight of 2,6 - difluoro - 3,5 - dichloro - 3',5' - dinitro - 6' - methyl - 4,2' - bispyridylamine, based on the combined weight of the said bispyridylamine and the film-forming material.

21. A coating composition according to Claim 11 wherein the composition contains from 5 to 50% by weight of bispyridylamine, based on the combined weight of the bispyridylamine and the film-forming material.

13. A coating composition according to Claim 12 wherein the composition contains from 5 to 25% by weight of bispyridylamine, based on the combined weight of the bispyridylamine and the film-forming material.

14. A coating composition substantially as described with reference to Example 2.

15. A coating composition substantially as described with reference to Example 3.

16. A method of protecting the hull of a vessel against the growth of marine organisms which comprises application to the hull of a composition according to any of the preceding claims.

J. S. ROBERTS,
Agent for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1978.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.